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(54) **Carbon dioxide addition in hydrocracking/hydroisomerization processes to control methane production**

(57) Methane is suppressed in a hydroisomerization process without substantial effect on light gas and light liquid yields when carbon dioxide is included with the

feed and a Group VIII non-noble metal or Group VI metal catalyst supported on alumina or silica-alumina.

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isomerization. Specifically, metal concentrations ranging from about 0.05 to about 20 wt%, preferably about 0.1 to 10 wt%, still more preferably 2.0 to 5.0 wt% may be used. For example, in a preferred catalyst the cobalt loading may be 1-4 wt%, and the nickel loading may be 0.1-1.5 wt%. A Group VI metal such as molybdenum also can be employed in amounts more or less than or equal to the non-noble Group VIII metal, e.g., 1.0 to 20 wt%, preferably 8-15 wt%, in all cases by total weight of catalyst.

The metals are impregnated onto or added to the support as suitable metal salts or acids, e.g., nickel or cobalt nitrate, etc. The catalyst is then dried and calcined in well known fashions.

The base silica and alumina materials used in this invention may be, for example, soluble silicon containing compounds such as alkali metal silicates (preferably where  $\text{Na}_2\text{O}:\text{SiO}_2=1:2$  to  $1:4$ ), tetraalkoxysilane, orthosilicic acid ester, etc.; sulfates, nitrates, or chlorides of aluminum alkali metal aluminates, or inorganic or organic salts of alkoxides or the like. When precipitating the hydrates of silica or alumina from a solution of such starting materials, a suitable acid or base is added and the pH is set within the range of about 6.0 to 11.0. Precipitation and aging are carried out, with heating, by adding an acid or base under reflux to prevent evaporation of the treating liquid and change of pH. The remainder of the support producing process is the same as those commonly employed, including filtering, drying and calcination of the support material. The support may also contain small amounts, e.g., 1-30 wt% of materials such as magnesia, titania, zirconia, hafnia, or the like.

A preferred support is an amorphous silica-alumina carrier, containing less than about 35 wt% silica, preferably about 2-35 wt% silica, more preferably 5 to 30 wt% silica, and having the following pore-structural characteristics:

Pore Radius (A)	Pore Volume
0-300	>0.03 ml/g
100-75,000	<0.35 ml/g
0-30	<25% of the volume of the pores with 0-300 A radius
100-300	<40% of the volume of the pores with 0-300 A radius

Such materials and their preparation are described more fully in U.S. Patent No. 3,843,509 incorporated herein by reference. The materials have a surface area ranging from about 180-400  $\text{m}^2/\text{g}$ , preferably 230-375  $\text{m}^2/\text{g}$ , a pore volume of 0.3 to 1.0 ml/g, preferably 0.5 to 0.95 ml/g, bulk density of about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

The feed materials that are isomerized with the catalyst of this invention are waxy feeds, i.e.,  $\text{C}_5+$ , preferably boiling above about 350°F (177°C) preferably above about 550°F (288°C) and may be obtained either from a Fischer-Tropsch process which produces substantially normal paraffins or from slack waxes. Slack waxes are the by-products of dewaxing operations where a diluent such as propane or a ketone (e.g., methylethyl ketone, methyl isobutyl ketone) or other diluent is employed to promote wax crystal growth, the wax being removed from the lubricating oil base stock by filtration or other suitable means. The slack waxes are generally paraffinic in nature, boil above about 600°F (316°C), preferably in the range of 600°F (316°C) to about 1050°F (566°C), and may contain from 1 to 35 wt% oil. Waxes with low oil contents, e.g., 5-20 wt% are preferred; however, waxy distillates or raffinates containing 5-45% wax may also be used as feeds. Slack waxes are usually freed of polynuclear aromatics and heteroatom compounds by techniques known in the art, e.g., mild hydrotreating as described in U.S. Patent No. 4,900,707, which also reduces sulfur and nitrogen levels preferably to less than 5 ppm and less than 2 ppm, respectively. Fischer-Tropsch waxes are preferred feed materials, having negligible amounts of aromatics, sulfur and nitrogen compounds.

Isomerization conditions usually include temperatures of 300-400°C, 500-3000 psig hydrogen, 1000-10,000 SCF/bbl hydrogen treat and space velocity of 0.1-10.0 LHSV. Preferred conditions include 320-385°C, 750-1500 psig hydrogen, 0.5-2 v/v/hr.

The catalyst is generally employed in a particulate form, e.g., cylindrical extrudates, trilobes, quadrilobes, and ranging in size from about 1-5 mm. The hydroisomerization can be carried out in a fixed bed reactor and the products may be recovered by distillation.

The following examples will illustrate this invention but are not meant to be limiting in any way.

All of the hydroisomerization studies were carried out in a small upflow pilot plant. The catalyst was evaluated at 750 psig, 0.50 LHSV, 690-700°F (366-377°C), and with a nominal  $\text{H}_2$  treat rate of 2500 SCF/B. A 10 cc charge of catalyst crushed and sized to 14/35 mesh was employed in each case. The catalyst comprised 15.2 wt%  $\text{MoO}_3$  and 3.2 wt%  $\text{CoO}$  on a silica-alumina Co gel with 20-30 wt% bulk silica. Balances were typically collected at 24-72 hour intervals. The reaction temperature was set to meet a target of 50% 700°F+ wax conversion and was not adjusted during the run. The Fischer-Tropsch wax employed in these studies had a nominal composition of 0.70% IBP-500°F (260°C), 20.48% 500-700°F (260-371°C), 78.82% 700°F+ (371°C). Typical run lengths were 800-1000 hours. Boiling range distributions for gas, naphtha, distillate range products, and lubes were obtained by a combination of simulated gas chromatography

Examination of the remaining products (e.g., C<sub>2</sub>-C<sub>4</sub>, C<sub>5</sub>-320°F (160°C), 320-500°F (160-260°C), 500-700°F (260-371°C) reveal little or no effect from the CO<sub>2</sub> other than differences attributed to the changes in conversion.

The following table illustrates the actual product yields for the CO<sub>2</sub> experiment.

Total Time On Run (Hours)	297.0	320.5	434.0	650.0	770.5
Delta Time	----	t=0	t=113.5	t=329.5	t=450
700°F+ Conversion	46.88	52.12	41.64	40.67	45.71
CH <sub>4</sub>	2.005	2.022	0.265	0.256	0.237
C <sub>2</sub> H <sub>6</sub>	0.196	0.190	0.033	0.037	0.043
C <sub>3</sub> H <sub>8</sub>	0.416	0.414	0.358	0.408	0.472
C <sub>4</sub> H <sub>10</sub>	1.140	1.182	1.054	1.289	1.555

t = 0 is the point at which carbon dioxide was added

These data were taken after line-out had been achieved.

From the table it is clear that C<sub>1</sub> (methane) was substantially suppressed; C<sub>2</sub> was suppressed somewhat, C<sub>3</sub> and C<sub>4</sub> were virtually unaffected and as a result C<sub>2</sub>-C<sub>4</sub> was substantially unaffected. Additionally, total conversion was suppressed at the outset of CO<sub>2</sub> addition, and recovered somewhat as the reaction proceeded. Thus, C<sub>2</sub>-C<sub>4</sub> cracked products can range from about 1 wt% to about 3 wt%.

### Claims

1. A hydroisomerization process in which CH<sub>4</sub> yields are suppressed without substantial effect on other light hydrocarbon yields which comprises reacting at hydroisomerization reaction conditions a C<sub>5</sub>+ paraffinic feedstock in the presence of hydrogen and carbon dioxide and a catalyst comprising a Group VIII non-noble metal or a Group VI metal or both supported on alumina or silica-alumina.
2. The process of claim 1 wherein the carbon dioxide is present in amount of at least about 0.2 mole % based on feed.
3. The process of claim 1 or claim 2 wherein the carbon dioxide is present in amounts in the range of about 0.3 to 1.0 mole %.
4. The process of any one of claims 1 to 3 wherein the catalyst contains at least one Group VIII non-noble metal oxide and at least one Group VI metal oxide.
5. The process of any one of claims 1 to 4 wherein a Group VIII metal is cobalt of the catalyst and a Group VI metal of the catalyst is molybdenum.
6. The process of any one of claims 1 to 5 wherein the support is a silica-alumina support and the silica is less than about 35 wt% of the support.
7. The process of any one of claims 1 to 6 wherein the support contains from about 2-30 wt% silica.
8. The process of any one of claims 1 to 7 wherein the surface area of the support is in the range of from about 180-400 m<sup>2</sup>/gm.
9. The process of any one of claims 1 to 8 wherein the total conversion of the feed is in the range of from about 30-70%.
10. The process of claim 1 comprising recovering from the catalytic hydroisomerization step an isomerized product having a methane content of less than about 1 wt% on feed.

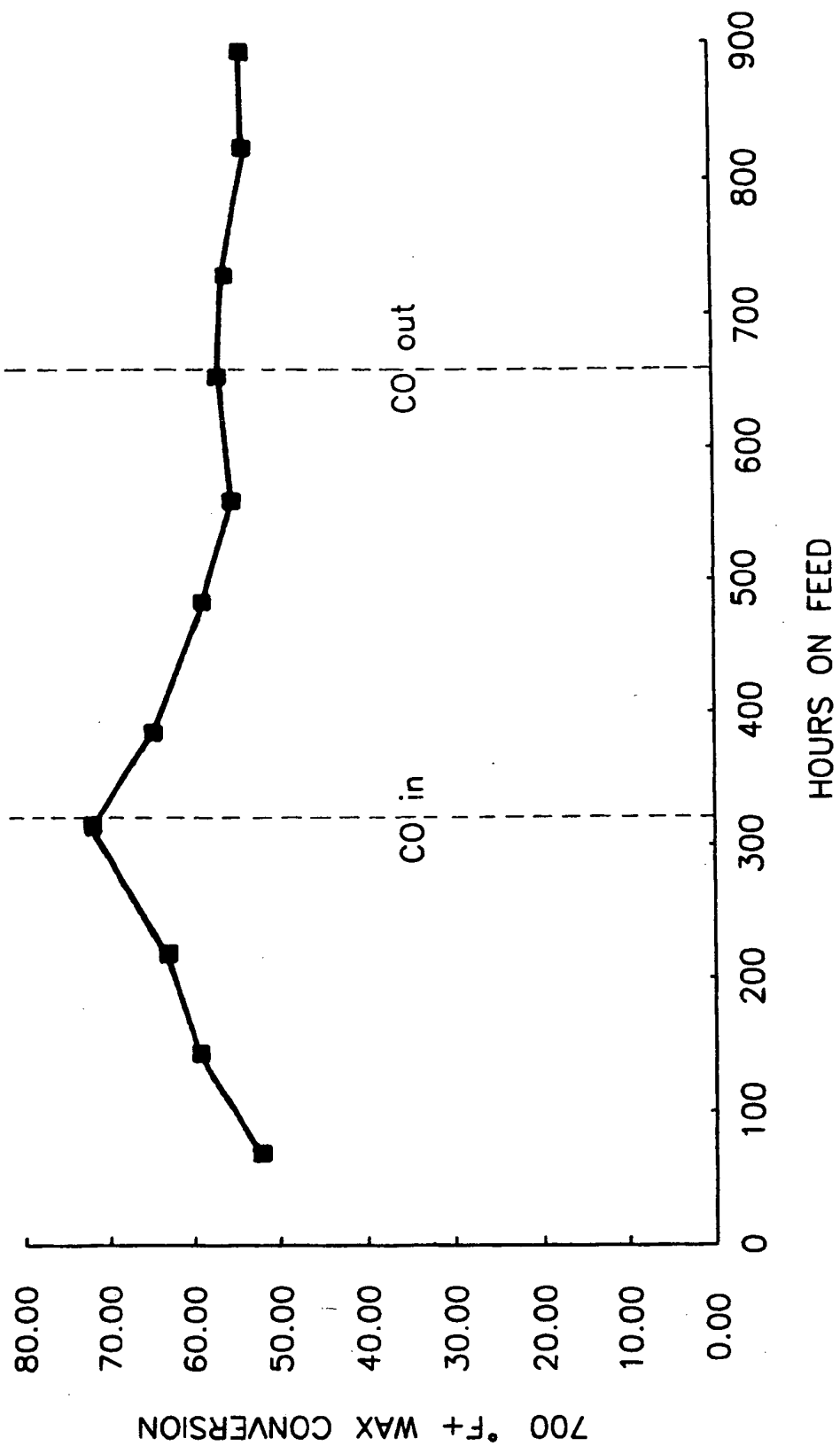


FIG. 1a

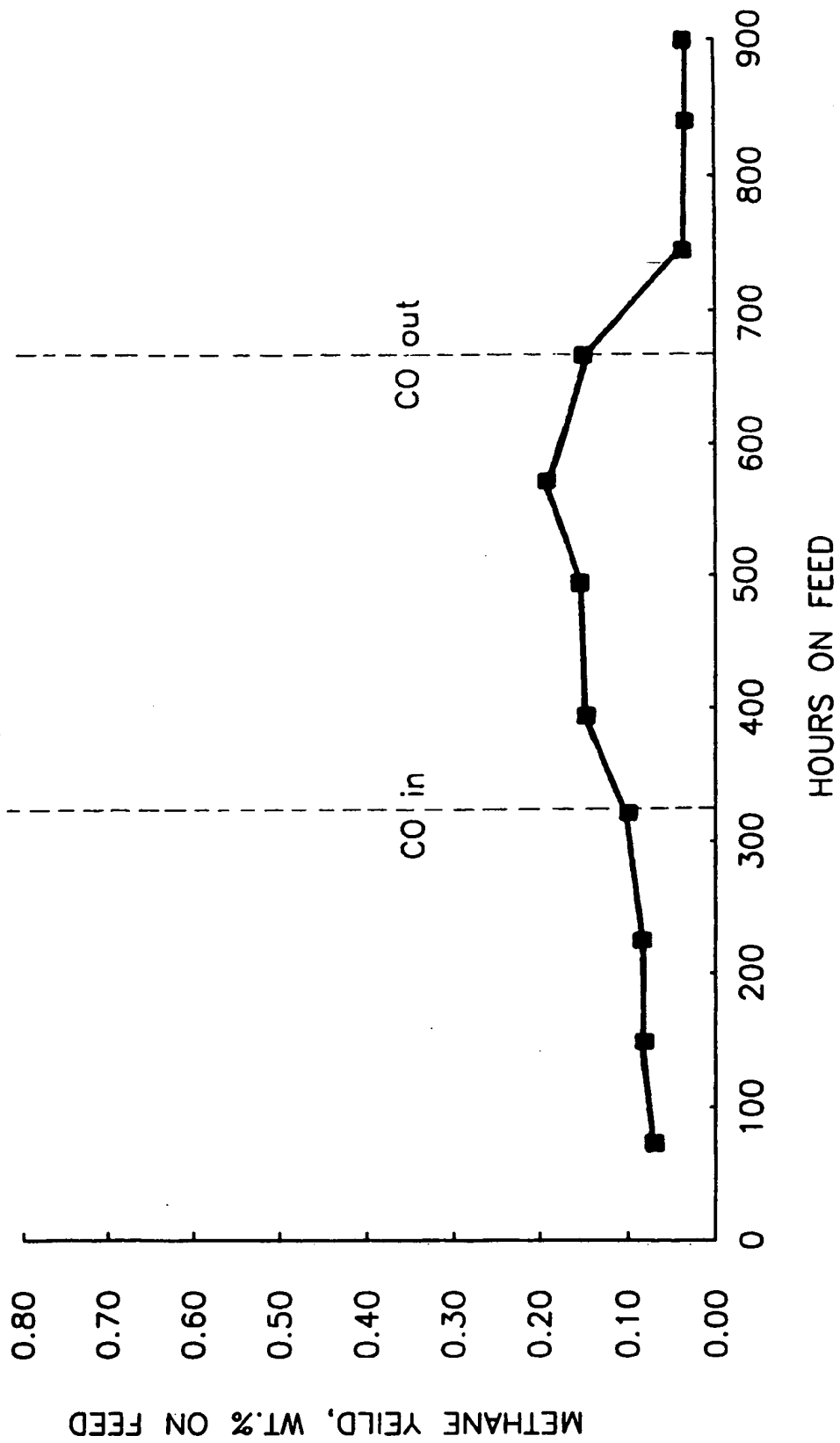


FIG. 1b

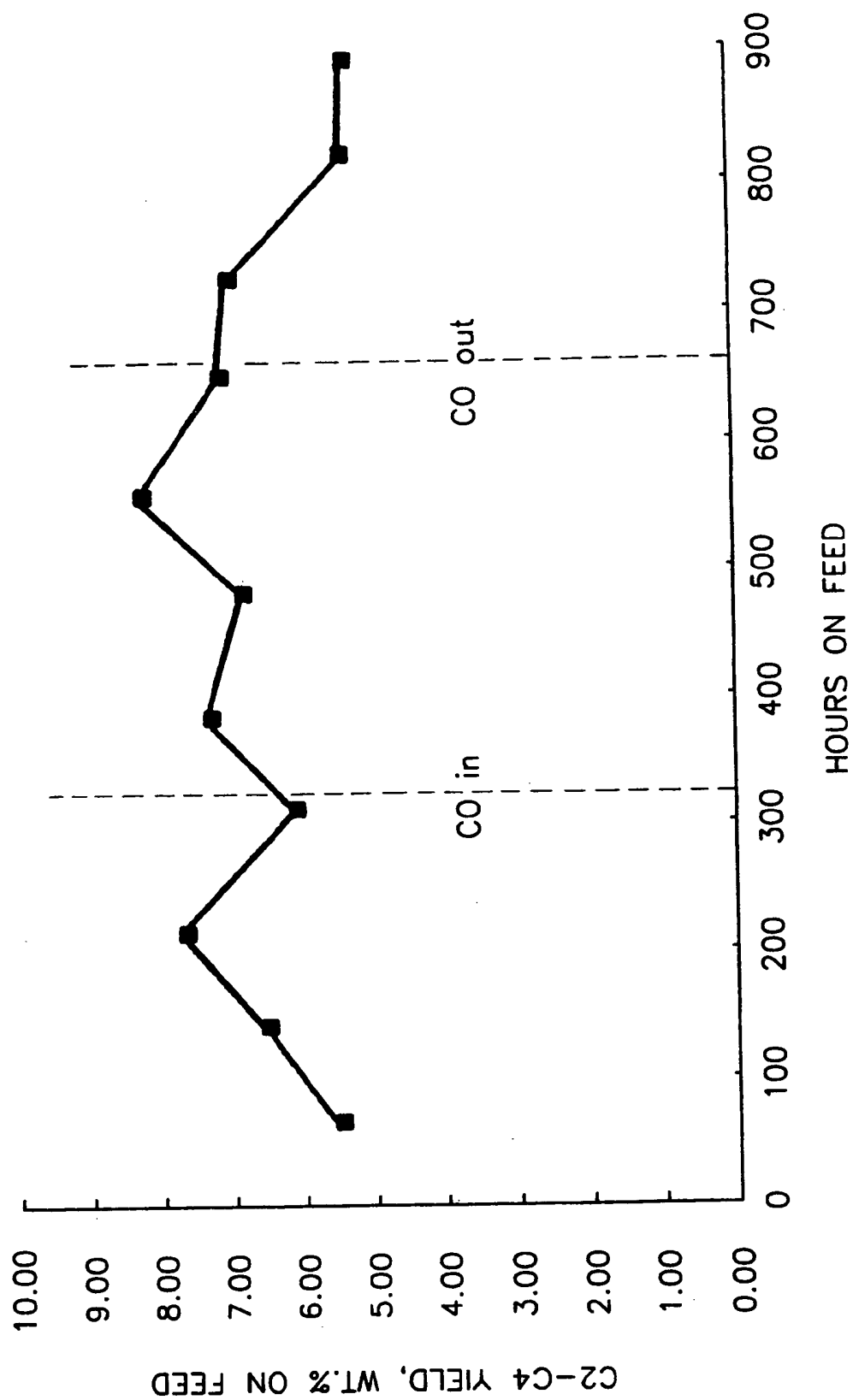


FIG. 1c

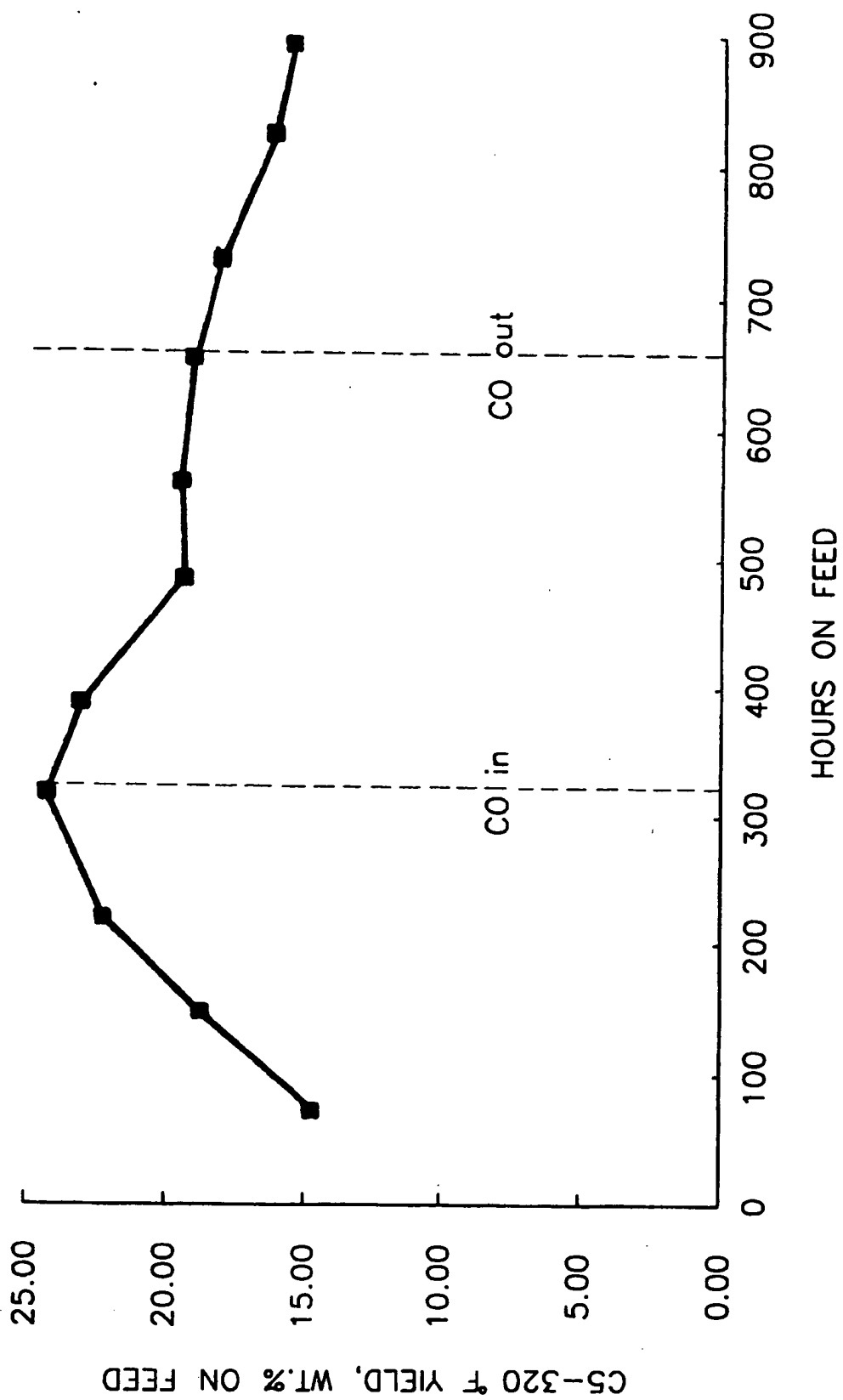


FIG. 1d

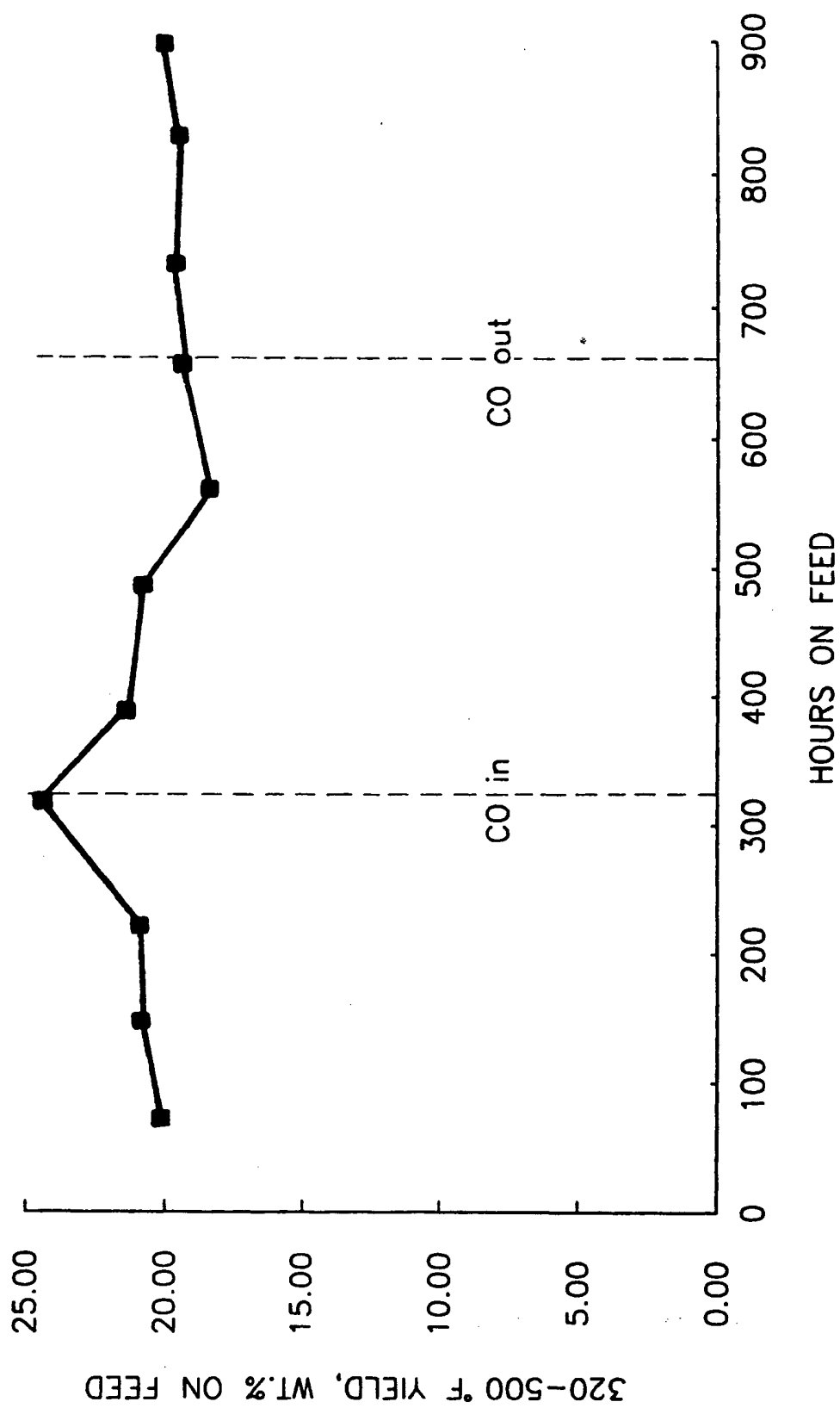


FIG. 1e

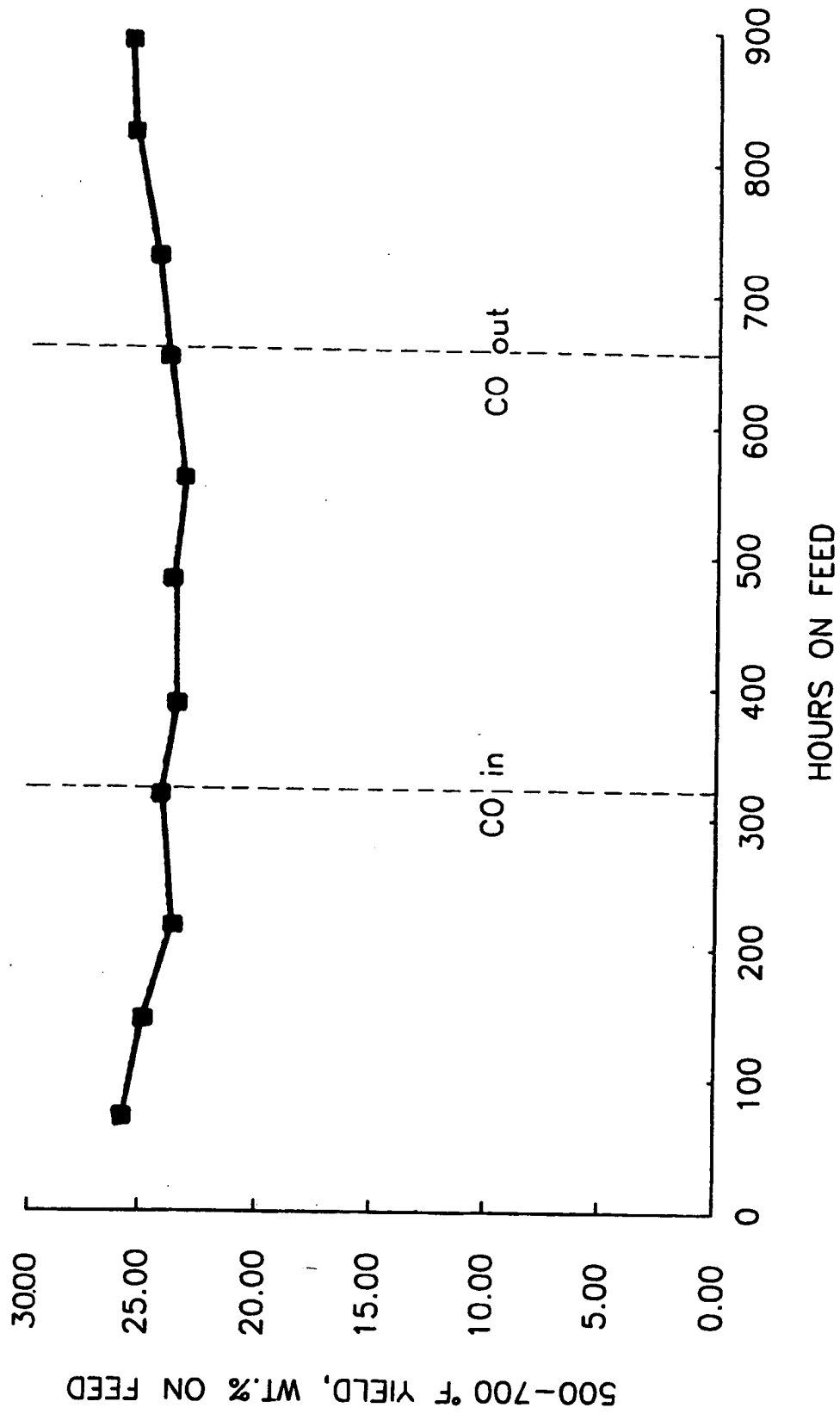


FIG. 1f

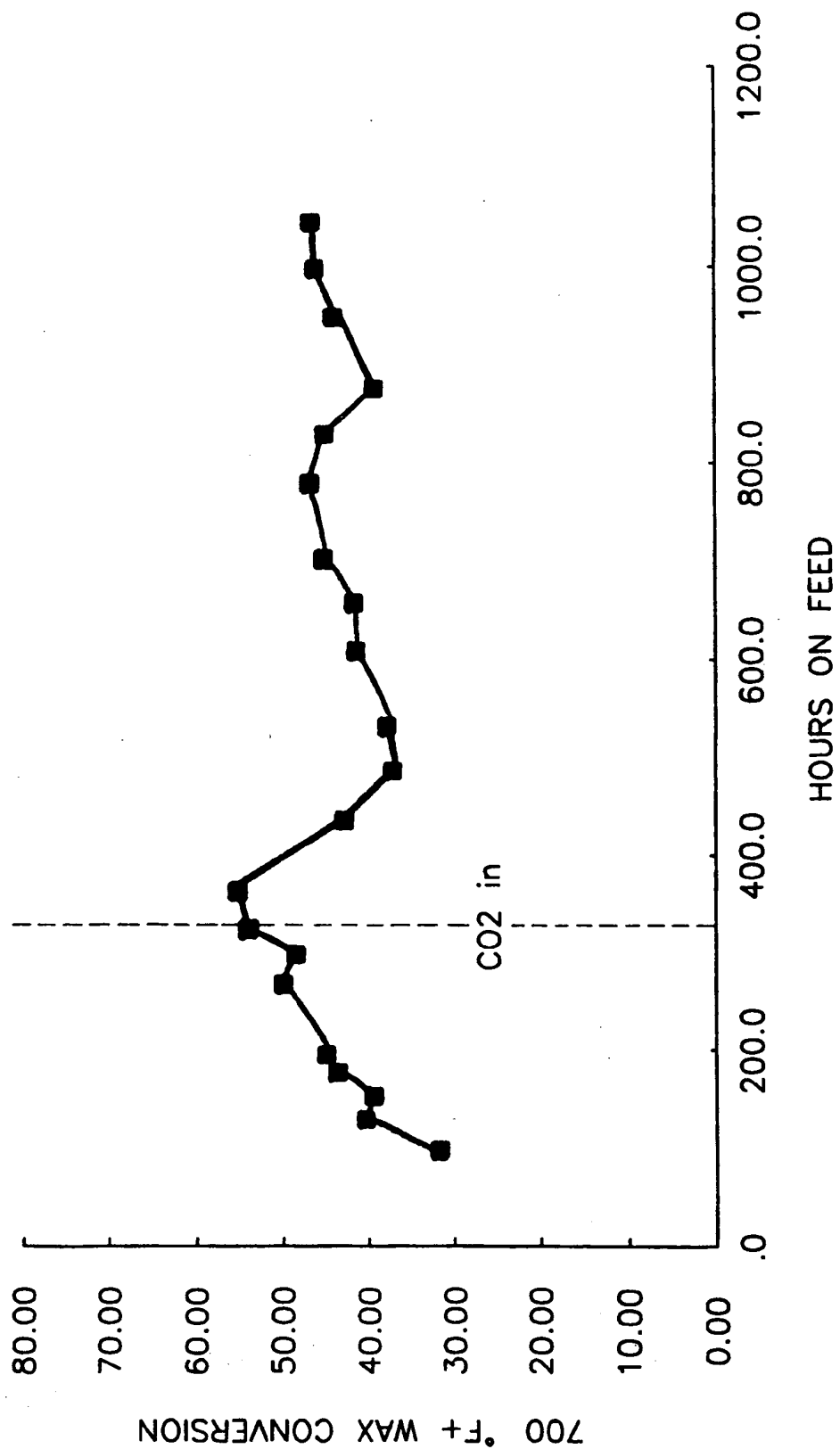


FIG. 2a

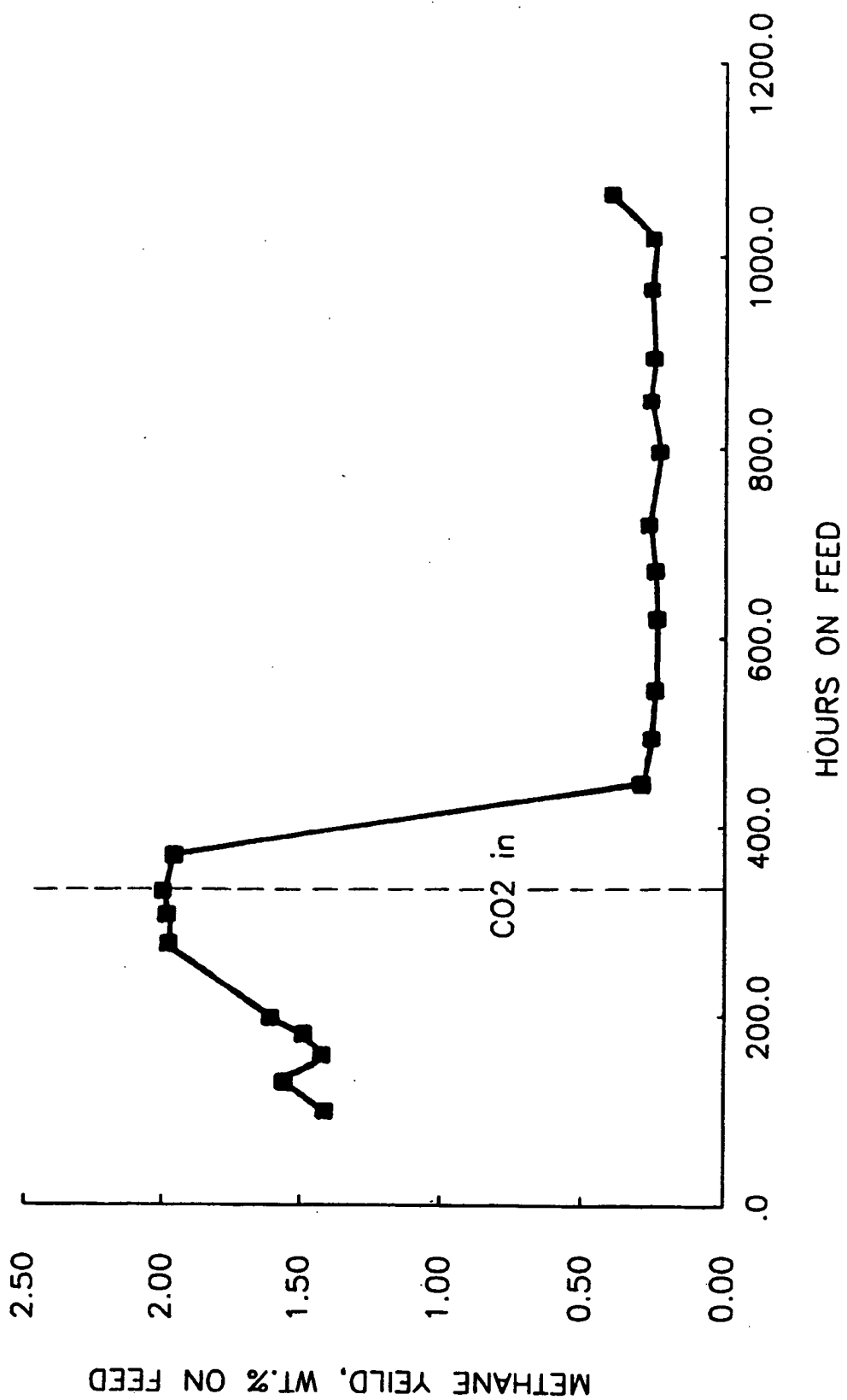


FIG. 2b

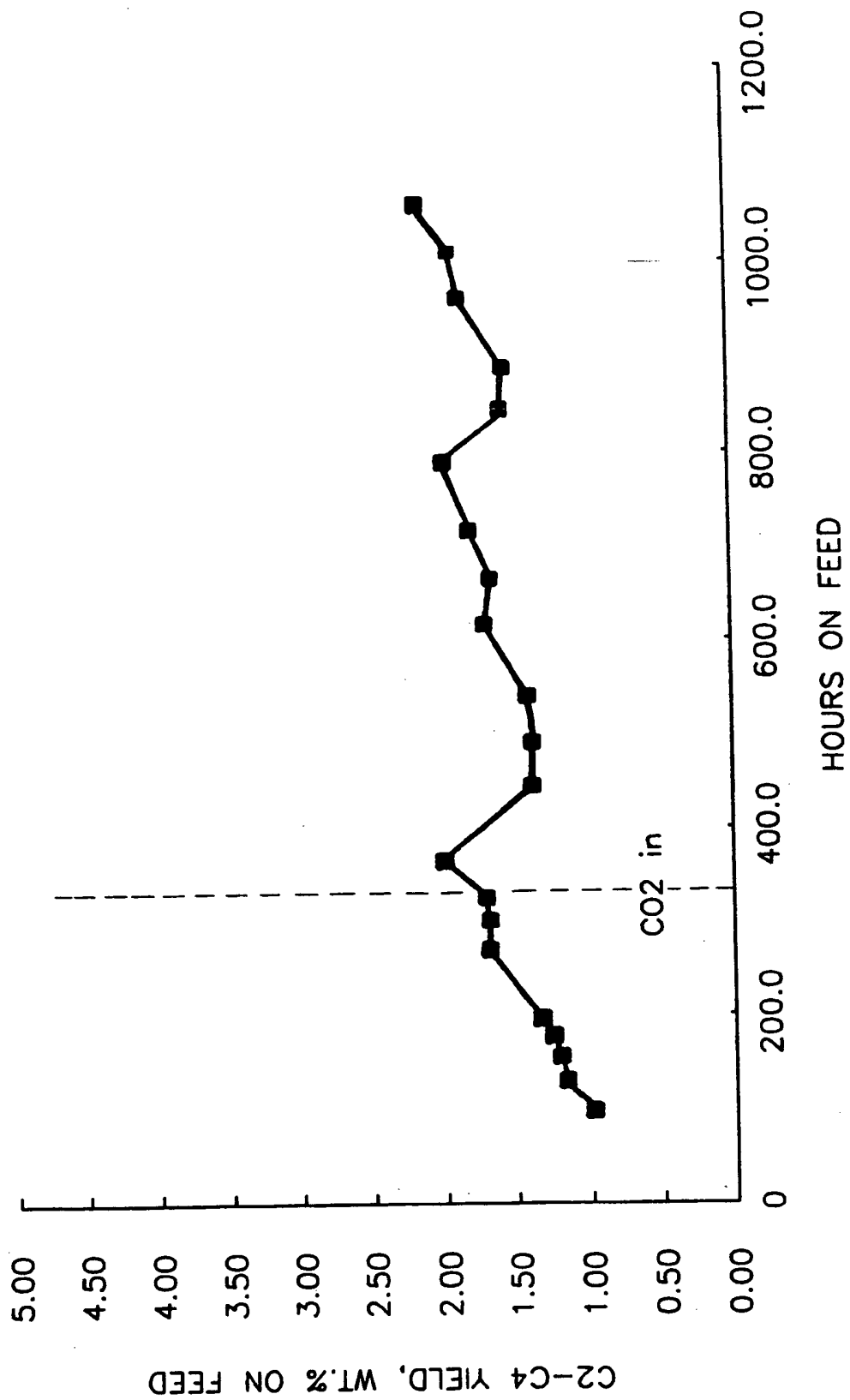
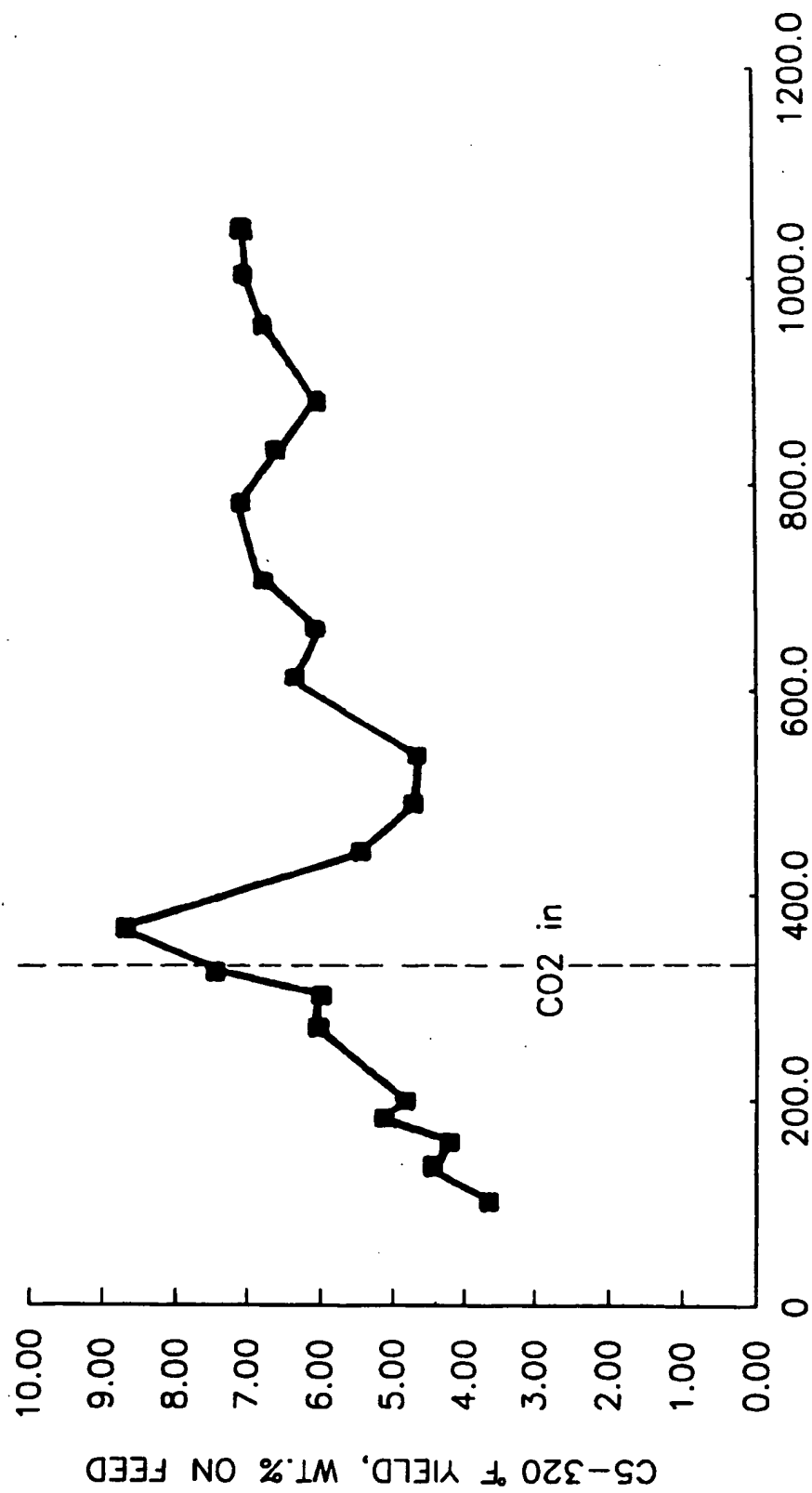


FIG. 2C



HOURS ON FEED

FIG. 2d

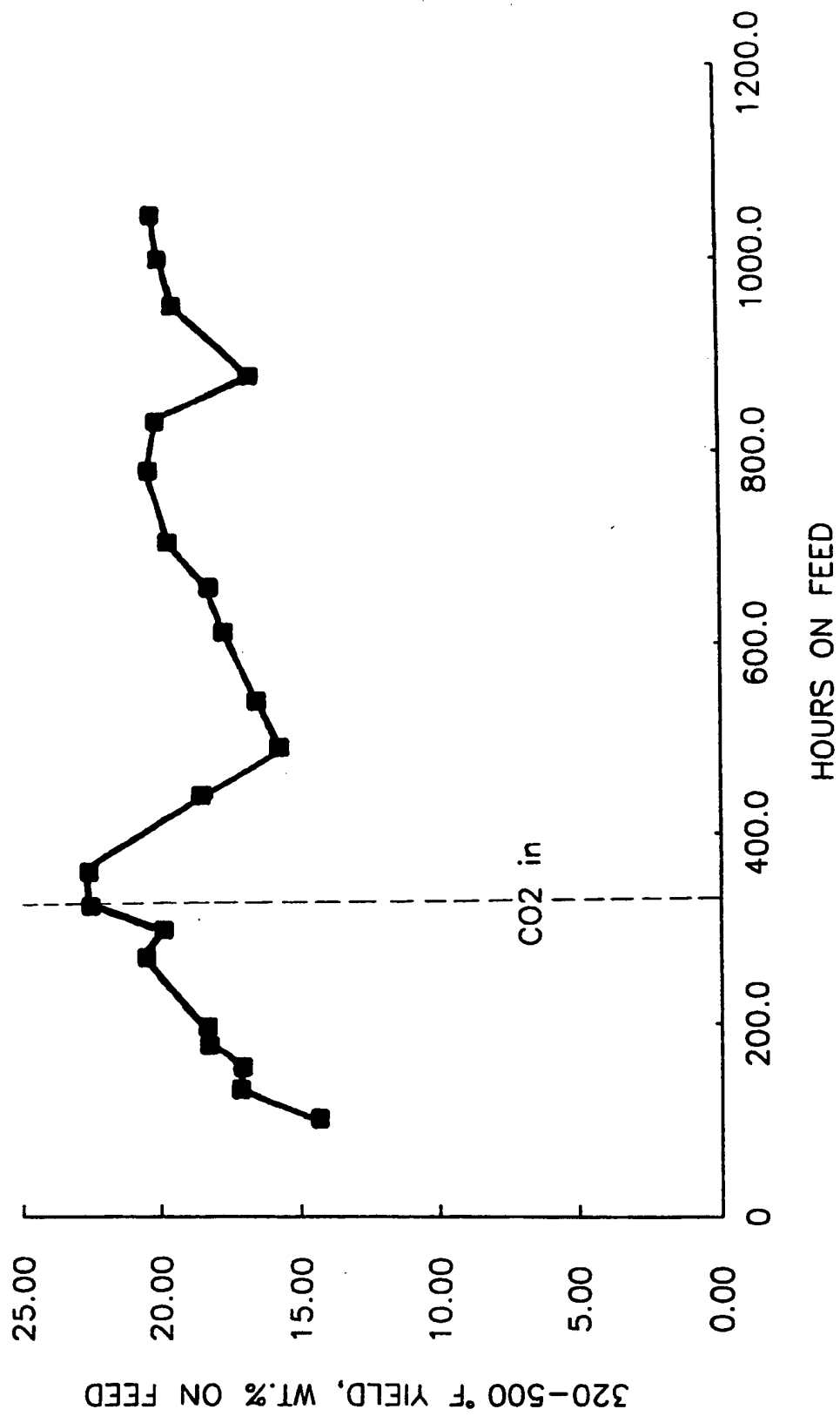


FIG. 2e

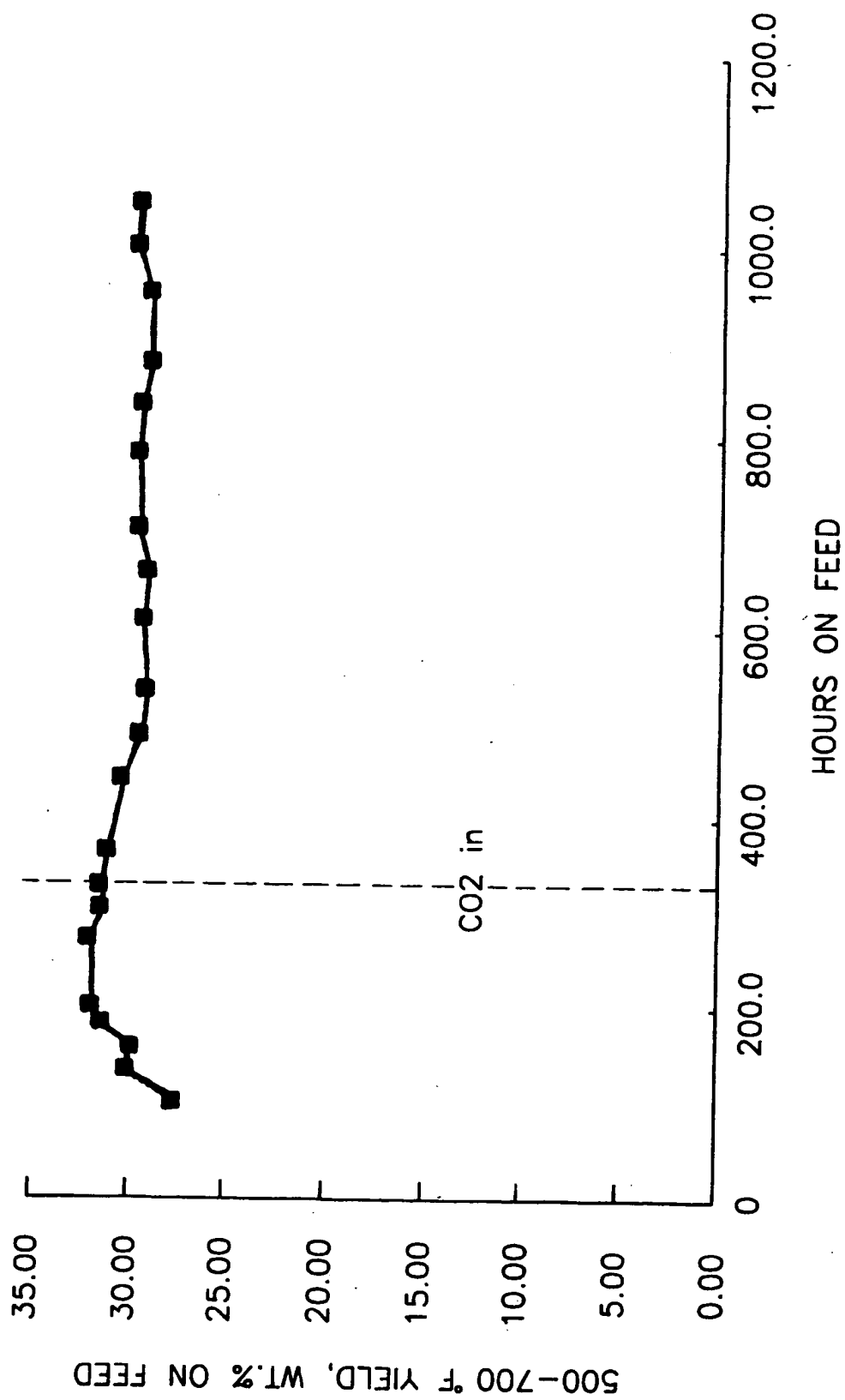


FIG. 2f



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# EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 5724

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	GB-A-772 478 (GULF) * the whole document *	1-10	C10G45/58
D,A	US-A-3 711 399 (TEXACO)		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C10G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 November 1995	Examiner Michiels, P
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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